Some properties of fullerenes and carbon nanotubes

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ABSTRACT

Experiments on preparation of $\text{C}_{60}\text{ONCF}_n$ cycloadduct ($\text{Fn}=\text{ferrocene}$) and $\text{C}_{60}(\text{Cocp}_2)_3$ charge transfer complexes are described and their properties analyzed. The ferrocene derivative is bound to $\text{C}_{60}$ at the 6-6 bond by a heterocyclic oxygen-nitrogen-carbon ring. The experimental results are compared with the results of modeling using semiempirical quantum chemistry PM3 model.

Scanning tunneling microscopy and spectroscopy has been used to observe variation of electronic structure along capped carbon nanotubes deposited on freshly cleaved HOPG(0001) surface. The electronic structure has been derived from measured dependence of tunneling conductance $dI/dV$ on the applied voltage. Evolution of $dI/dV(V)$ along the nanotube are discussed in terms of existing theories of nanotubes and quantum chemistry calculations.

Keywords: fullerenes, adducts, charge transfer, carbon nanotubes, STM,

1. INTRODUCTION

Discovery of an efficient method of fullerenes production in the electric arc\textsuperscript{1} following their detection\textsuperscript{2} not only allowed investigation of pure fullerenes but also opened a field of the fullerenes chemistry. One of the first experimental tasks was verification of the cage structure of fullerenes proposed by Smalley et al.\textsuperscript{2}. The most common fullerene $\text{C}_{60}$ consists of 60 carbon atoms arranged on a sphere of 7.1 Å diameter. The atoms form twenty hexagons and twelve pentagons, there are two types of C-C bonds: at the pentagon-hexagon and hexagon-hexagon border equal to $d_{5-6}=1.46$ Å and $d_{6-6}=1.4$ Å, respectively\textsuperscript{3}. The two types of bonds are often considered as single and double ones.

At the early stage of investigations it was supposed that fullerenes ought to be chemically inactive and relatively stable. However it has been later proved that fullerenes participate in various chemical reactions. Their chemical activity results from an easy breakage of one of the double bonds; in later experiments a way to break single bonds has been found thus allowing preparation of various types of $\text{C}_{60}$-adduct compounds.

Fullerenes proved also to be strong acceptor of electrons in presence of many in- or -organic donors. This property does not result as much from low energy of LUMO (Lowest Unoccupied Molecular Orbital) of the neutral fullerene that may accept charge from the donor but rather from fullerene geometrical structure allowing distribution of the acquired charge over large volume thus diminishing electrostatic interaction at the donor site.

Discovery of carbon nanotubes\textsuperscript{8} was a consequence of revived interest in electric arc generated between graphite electrodes after Krätchmer’s experiments. They were found in carbon deposits grown on the cathode in the arc. Carbon nanotubes consist of single or many concentric rolled graphene sheets. The carbon atoms remain arranged in hexagons with C-C distance close to 1.42 Å, the distance between the walls in multi-wall nanotubes is close to that in graphite i.e. 3.41 Å. The diameter of nanotubes is in the range from 1 nm to hundreds of nm, they may be many microns long. The symmetry of nanotube depends on carbon hexagons arrangement relatively to the nanotube axis. The symmetry so strongly influences the nanotube’s electric properties that they may have either metallic or semiconducting electric conductivity\textsuperscript{9-11}. It is expected that carbon nanotubes may be applied as electron emitters at low temperatures, scanning tunneling microscope tips or even be used for resilient, wear resistant fabrics. The two first fields of application results from the nanotubes geometrical structure while the third from the C-C bonds considered to be the strongest in Nature.
Here we will present results of experiments on preparation of ferrocene derivative adduct to fullerene C$_{60}$, C$_{60}$: cobaltocene charge transfer complexes aimed to dope fullerides with transition metals. The experiments will be interpreted using semiempirical quantum chemistry modeling. In the second part tunneling spectroscopy measurements of carbon nanotubes will be presented and results will be compared with calculations based on semiempirical quantum chemistry.

2. C$_{60}$ adduct

Because of high melting temperature and low vapor of iron it cannot be diffused into the fullerite lattice, therefore we searched for chemical methods of doping C$_{60}$ with the metal. In our previous publications$^{12-14}$ several reactions between fullerenes and ferrocene (Fn=Fe(η$_5$-C$_5$H$_5$)) used as a source of the metal was described. Ferrocene at normal conditions does not react with C$_{60}$. The process had to be carried out either at high temperatures by decomposing ferrocene dissolved in the solid fulleride or at low temperatures in the solution using catalysts. These processes lead to the contamination of fullerenes by hydrocarbon impurities that had to be later removed by vacuum annealing. Various experimental methods like X-ray diffraction, Mössbauer spectroscopy; thermal analyses, magnetic susceptibility and ESR were applied to determine properties of those samples$^{15-19}$.

The adduct was prepared by a chemical method in a three-step process using C$_{60}$ and ferrocenecarboxaldehyde (FnCHO) as the substrates. In the first step the ferrocenecarboxaldehyde FnCHO was transformed to ferrocenecarboxaldehyde oxime (FnCH=NOH). The FnCHO and hydrochloride hydroxylamine NH$_2$OH.HCl were dissolved in ethanol. To the solution sodium hydroxide NaOH was successively added maintaining solution at boiling temperature for two hours. Then the solution was cooled and water was added to promote precipitation of the reaction products, the ferrocenecarboxaldehyde oxime remained in the solution. The product C$_{60}$ONCFn was separated by a chromatography method using silica gel column with toluene as an eluent$^{20}$.

The cycloaddition of ferrocene nitrile oxide FnC≡N'O to fullerene employed proceeds according to the scheme:

\[
\text{FnCHO} \quad \xrightarrow{\text{NH}_2\text{OH}*\text{HCl}} \quad \xrightarrow{\text{NaOH}} \quad \xrightarrow{\text{NCS}} \quad \xrightarrow{\text{CH}_3\text{Cl}_2} \quad \left[\text{FnC}=\text{N'O}\right] \quad \xrightarrow{\text{C}_{60}} \quad \xrightarrow{\text{Et}_3\text{N}} \quad \xrightarrow{} \quad \text{C}_{60}\text{ONCFn}
\]

There are two possible structures of the fullerene monoadduct C$_{60}$ONCFn. The structures optimized with use of semiempirical method PM3 is presented in Fig.1. As shown, the molecule of ferrocene is bound to the fullerene at the 6-6 ring junction by isoxazoline (-C=N-O-) ring.

The $^1$H NMR exhibits one sharp resonance line with the chemical shift $\delta=4.20$ ppm and two lines at $\delta=4.53$ ppm and 5.20 ppm, the ratio of the intensity of the lines equals to 5:2:2. The number and relative intensities of the $^1$H NMR lines well correspond to the number of various positions of hydrogen atoms in both models presented in Fig.1 with one non-substituted ring where all the protons are equivalent and one singly substituted ring with two types of the proton sites. The $^{13}$C NMR spectrum includes resonance lines at $\delta=68.1$, 69.7, 69.8 ppm ascribed to cp; at $\delta=73.2$, 75.4, 102.7 ppm ascribed to cp or to C in isoxazoline ring and 28 lines in the range of $\delta=135.2 \div 152.4$ ppm ascribed to C$_{60}$. Number and positions of the $^1$H and $^{13}$C NMR lines correspond with both presented structures.

The IR absorption spectra were measured in the wavenumber range of 400-3000 cm$^{-1}$ using FT-IR Perkin Elmer 1725X spectrometer in order to obtain further information on the compound. The pellets were prepared from the mixture of the dried C$_{60}$ONCFn sample with the KBr powder.

![Figure 1](image.png)

Figure 1. Two possible structures of C$_{60}$ONCFn compound, with almost the same heat of formation, optimized using the PM3 model. The reaction breaks one of the double C-C bonds on fullerene increasing its length 1.596 Å.
The large number of the observed absorption lines does not allow for an unambiguous assignment of each of them. However, the IR active modes characteristic to \(\text{C}_6\text{O}\) and to the ferrocene could be identified in the spectrum. The four IR active \(\text{C}_6\text{O}\) modes could be distinguished, though their relative intensities differ from those observed in pure \(\text{C}_6\text{O}\) spectra here the tangential mode at 527 cm\(^{-1}\) is the most intense one. Some of the absorption lines coincide with those observed in pure \(\text{C}_6\text{O}\) ascribed in \(^{21}\) to the modes activated by the symmetry lowering, here the \(\text{C}_6\text{O}\) symmetry is lowered by the adduct. The ferrocene IR absorption lines are shifted to higher energies in comparison to pure ferrocene. The tentative assignment of some of the absorption lines to the vibrations of the main components of the complex is listed in Table 1. The first two columns contain position of the observed absorption lines (in cm\(^{-1}\)) ascribed to: 1. pure \(\text{C}_6\text{O}\), and 2. \(\text{C}_6\text{O}\) modes activated by the adduct, respectively. The interpretation of the vibrational modes is given in the third column and positions of calculated strong lines are listed in the last two columns (for the adduct shown in left part of Fig.1).

### Table 1. List of characteristic IR modes position (in cm\(^{-1}\)) observed and calculated in \(\text{C}_6\text{O}\) and \(\text{C}_6\text{O}\text{ONCFn}\).

<table>
<thead>
<tr>
<th>Observed</th>
<th>Interpretation</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_6\text{O})</td>
<td></td>
<td>(\text{C}_6\text{O})</td>
</tr>
<tr>
<td>deformed (\text{C}_6\text{O})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-cp stretch</td>
<td></td>
<td>602-629</td>
</tr>
<tr>
<td>cp tilt</td>
<td></td>
<td>483-542</td>
</tr>
<tr>
<td>527</td>
<td>(\text{C}_6\text{O}) cage deformation</td>
<td>557</td>
</tr>
<tr>
<td>543, 563</td>
<td></td>
<td>542-556</td>
</tr>
<tr>
<td>576</td>
<td>(\text{C}_6\text{O}) symmetric breathing</td>
<td>733</td>
</tr>
<tr>
<td>750, 959</td>
<td>(\text{C}_6\text{O}) asymmetric deformation</td>
<td>500-750</td>
</tr>
<tr>
<td>C-H out of plane bend</td>
<td></td>
<td>800-900</td>
</tr>
<tr>
<td>C-H in plane bend</td>
<td></td>
<td>1000-1200</td>
</tr>
<tr>
<td>cp symmetric deformation</td>
<td></td>
<td>1254-1364</td>
</tr>
<tr>
<td>1182</td>
<td>(\text{C}_6\text{O}) pentagons asymmetric deformation.</td>
<td>1377</td>
</tr>
<tr>
<td>1156, 1168, 1215</td>
<td>(\text{C}_6\text{O}) pentagon and cp asymmetric deformation.</td>
<td>1378-1439</td>
</tr>
<tr>
<td>C-O stretch</td>
<td></td>
<td>1267-1288</td>
</tr>
<tr>
<td>C-C stretch, (\text{C}_6\text{O}) pentagons deformation</td>
<td>1693-1742</td>
<td></td>
</tr>
<tr>
<td>1428</td>
<td>(\text{C}_6\text{O}) pentagon pinch</td>
<td>1708</td>
</tr>
<tr>
<td>C=O</td>
<td></td>
<td>1640, 1838</td>
</tr>
<tr>
<td>C-H stretch</td>
<td></td>
<td>3162-3195</td>
</tr>
</tbody>
</table>

Figure 2. Thermogravimetric and differential scanning calorimetry plots of the complex.

Figure 3. Fragment of the \(\text{C}_6\text{O}\) fcc (111) plane with two \(\text{C}_6\text{O}\text{Fe}\) complexes. The shaded area around one complex depicts constant charge density lines in [\(\text{e} \cdot \text{Å}^3\)] (from 0 step 0.03 to 0.45).
The most characteristic lines in the observed spectrum relatively well coincide with the calculated ones. Yet it ought not to be considered as prove of the structure.

Since our intention was preparation of fulleride with dissolved iron in the lattice, we have carried out thermal analyses to determine conditions of the decomposition of the compound using Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) methods. The experiments were carried out at 10°C/min heating rate in helium atmosphere. There are three overlapping endothermic peaks in DSC scan shown in Fig. 2 in the temperature range 100-200 °C; they are connected with 8% weight loss observed by TG method. The effects may be ascribed to evaporation of toluene and free ferrocene derivative. We ascribe the single step process observed at 330°C by both methods to the decomposition of the cycloadduct. The observed 15% weight loss is comparable with the expected loss of 18% if C60 and C60CNO were freed from the C60-ONCFn complex and evaporated. Then an endothermic peak in the DSC scans should be expected in this temperature region because of the energy required to break the C60 -ONCFn and cp-Fe-cp ferrocene bonds while in the experiment the exothermic effect appears. It may be explained assuming dimerization or polymerization of the freed fragments if the heat released in the process prevailed over the endothermic processes. We suppose that chemically inactive polymers evaporate from the sample leaving most of iron in the fulleride. According to the X-ray fluorescence analyses iron at the concentration of 0.85Fe/60C remains in the annealed samples.

We were unable to determine position of iron atoms in the lattice after annealing the samples because fullerenes returned to the fcc structure with the lattice constant increased only by 1% in comparison with the pristine fulleride. It may be supposed that between C60 molecules remains enough space to accommodate dissolved iron. According to the molecular modeling using the PM3 approximation in the most stable C60Fe complex iron atom is located opposite to one of the hexagons. The distance from the hexagon is so small that C60Fe complexes may fit in the fcc lattice if Fe was facing the interstitial sites as shown in Fig. 3. The C60Fe samples exhibit superparamagnetic properties.

3. Charge transfer complex C60(Cocp2)

Cobaltocene Cocp2 is chemically more active because there are more than eighteen electrons populating the molecular orbitals, therefore the compounds may donate electrons. It was proved by ESR experiments that cobaltocene indeed behaves as a donor in the presence of fullerene further, cobaltocene doped C60 exhibits ferromagnetism ascribed to the unpaired spins residing on fullerene. We have found that fullerene and cobaltocene react immediately in toluene at the relative concentration C60:Cocp2 = 1:3 molar ratio. Both components precipitate leaving colorless solvent; it is insoluble in standard organic solvents. The dried precipitate was used for further experiments aimed to determine its molecular structure and character of the reaction. The powder had an amorphous structure according to X-ray and electron diffractions thus we have no experimental information on the structure of the reaction product. By the mass spectrometry measurements only fragments of molecules constituting the sample and toluene were revealed but the experiment did not prove the existence of whole C60(Cocp2)n complexes.

As in case of C60ONCFn adduct we have used semiempirical quantum chemistry model PM3 to gain insight into the bonds between the fullerene and cobaltocene. We tried to optimize various C60(Cocp2)n complexes in the unrestricted and restricted Hartree-Fock approximation. The calculations were performed for the whole complexes consisting of the fullerene and cobaltocene molecules; neither any additional bonds nor charge transfer were imposed at the beginning of optimization. It results from the calculations that complexes C60(Cocp2)n with n=1,2,3 may exist though the binding energy is relatively low, in case of C60(Cocp2)3 the binding...
energy equals to 1.2 kcal/mol relatively to the isolated molecules. The structure of the optimized complex is shown in Fig. 4. The most distant cobalt atoms are separated by 1.41 nm and hydrogen atoms closest to C\(_{60}\) are only 0.17 nm apart from carbon atoms constituting fullerene, i.e. less than expected if the molecules did not interact with C\(_{60}\). In the isolated cobaltocene, ligands always remain neutral according to this calculation method, while here fullerene acquires the charge equal to 2.44e donated by the cyclopentadiens (cp). The energy distribution of the MO in isolated C\(_{60}\), Cocp\(_2\) and C\(_{60}\)(Cocp\(_2\))\(_3\) is shown in Fig. 5.

It is often assumed that for the charge transfer to occur HOMO of the donor has to be above LUMO of the acceptor, however here in the isolated Cocp\(_2\) molecule HOMO lays below the C\(_{60}\) LUMO thus the charge transfer would require higher electronic energy, total energy would also increase if the charged molecules were separated. The coulombic interaction between the charged molecules at close distance lowers HOMO of the complex (see Fig. 5) that is composed essentially of the C\(_{60}\) \(t_{1u}\) orbitals. The donated electrons occupy molecular orbitals located mainly on C\(_{60}\) yet overlapping the three Cocp\(_2\). Because the three degenerate \(t_{1u}\) MOs extend along the axis therefore Cocp\(_2\) positioned at opposite sides of C\(_{60}\) can only couple with the same \(t_{1u}\) MO thus such complex can be in doublet rather than in a quartet state. The computational analyses presented here demonstrate insufficiency of simple analyses based on redox potentials of the interacting molecules that cannot account for the deformation of interacting molecules and electrostatic interaction.

Only very few information on the structure of the compound may be directly gathered from the infrared absorption (IR) because the spectrum - shown in Fig. 6 - consists of broad and not well-defined lines. The lines at 462.8, 866.1, 1012.4 and 1069.2 cm\(^{-1}\) appear at wavelengths that might be ascribed to vibrations occurring in the organometallic complexes though their width and position differ from those observed in pure compounds, there also do not exist absorption directly ascribable to C\(_{60}\). It proves that there exists interaction between substrates in the compound. One may try to verify the model presented in Fig. 4 calculating vibration of the complex and comparing it with the experimental spectrum. The results of the calculations are presented in Fig. 7. The top panel shows vibrations of Cocp\(_2\) and the middle one of C\(_{60}\). The bars at the bottom of each panel show also positions of IR inactive modes. The lowest panel shows IR active modes of the complex; since there are many vibrations within this wavelength range here the intensities of vibrations of similar type, close in energy have been added up and represented by one bar. The whole groups of calculated transitions occur close to the wavelengths where absorption in the sample has been observed. Interpretation of the lines based on computer visualization agrees with generally accepted interpretation of vibrational absorption observed in other organic or organometallic compounds. The observed/calculated lines at 462/415, 503/474 and 527/479 cm\(^{-1}\) may be tentatively ascribed to deformed C\(_{60}\), Cocp\(_2\) and C\(_{60}\), respectively; the broad bands at 583.5/515 and 669/579 cm\(^{-1}\) to C\(_{60}\) and Co parallel to cp plane.

Figure 6. IR transmittance of C\(_{60}\)(Cocp\(_2\))\(_3\) sample: upper plot the fresh and lower annealed to 400°C sample.

Figure 7. Calculated IR absorption in Cocp\(_2\), C\(_{60}\) and C\(_{60}\)(Cocp\(_2\))\(_3\).
vibrations. The absorption in the range of 700-866/675-875 cm\(^{-1}\) might correspond to superimposed \(\text{C}_{60}\) radial deformation and CH out of plane vibrations. The next group beginning at 1012/1039 cm\(^{-1}\) and extending to 1069/1235 cm\(^{-1}\) originates predominantly from C-H out of plane and C-C in cp plane vibrations. The band from 1250 to 1500/1251-1500) cm\(^{-1}\) may originate from C-C asymmetric stretching in both \(\text{C}_{60}\) (tangential mode) and cp. The band with maximum at 1582 cm\(^{-1}\) corresponds to the peak at 1660 cm\(^{-1}\) that represents several transitions in the range 1520-1800 cm\(^{-1}\) originating from vibrations of deformed \(\text{C}_{60}\). It may be concluded that measured IR absorption does not contradict the optimized structure of Fig. 4.

Annealing of the \(\text{C}_{60}(\text{CoCp}_2)\), sample leads to decomposition of organic groups and their evaporation leaving \(\text{C}_{60}\text{Co}_3\) compound. The IR spectrum shown in Fig. 6 indicates that the sample may still contain residual hydrocarbons.

### 4. Carbon nanotubes

Carbon nanotubes (CN) differ by arrangement of the carbon hexagons in relation to their axis. If the hexagons are arranged as shown in Fig. 8A the CN is identified as an armchair one, in case of arrangement shown in Fig. 8C as a zigzag one. There is possible any other arbitrary arrangement of the hexagons in CNs as presented in Fig. 8B. The structure of CN is unambiguously described by the number of hexagons \(n\) in a single winding around CN and number \(m\) indicating shift along the axis. Thus for all zigzag CN \(m=0\) and all armchair CN \(n=m\).

It results from the band structure calculations performed in the tight binding approximation for the single wall CN that the energy gap is closed if \(n+2m=3q\) where \(q\) is an integer, in other cases the gap is open; it means that all armchair CN are metallic\(^9\)-\(^1\)\(^1\), \(^2\)\(^6\)-\(^8\). Molecular calculations applied to CN of various symmetries return distribution of Molecular Orbitals with the HOMO-LUMO gap also depending on the symmetry of CNs. These calculations additionally supply information on the states localized at the ends of CNs.

The extended Hückel approximation has been applied to calculate molecular states of closed at one end zigzag nanotube consisting of 640 carbon atoms. The structure of the nanotube was optimized using molecular mechanic model with the MM+ force field. It returns the C-C bond length equal to 1.4 Å, very close the measured distance 1.42Å.

Energy of the molecular orbitals close to the HOMO-LUMO gap is shown in Fig. 9 and spatial distribution of some molecular orbitals is shown in the following figure. It should be noted that the wave function extends over several neighboring atoms thus cannot be ascribed to very particular position e.g. to a single pentagon or hexagon. The energy of the states depends on geometry of the individual nanotube however the tendency to localization of the empty states at open end states is such that the wave function is localized by the ends of CN.

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**Figure 8.** Various orientations of carbon hexagons relatively to carbon nanotubes axis.

**Figure 9.** Energy distribution of MO of zigzag carbon nanotube.

**Figure 10.** Illustration of the molecular wave function localized by the ends of CN.
ends and of occupied states at closed ones occurs in many cases. It is possible to compare the calculations with the spectrum observed by tunneling spectroscopy along the nanotube. In particular, there may be unoccupied localized states observed at the open end of the tube or occupied at the closed end.

Scanning tunneling microscopy and spectroscopy has been used to observe variation of electronic structure along capped carbon nanotubes deposited on freshly cleaved HOPG(0001) surface. The sample has been prepared using a few µg’s of arc grown CN sonicated for 30 min. in 2 cm³ of dichloroethane. Then a droplet of the solution was deposited on freshly cleaved (0001) basal plane of highly oriented pyrolitic graphite (HOPG) surface, and then the sample has been dried in air. The STM image of two objects is shown in Fig. 11.

The electronic structure has been derived from measured dependence of tunneling conductance dI/dV on applied voltage. The constant current mode was established at the tunneling current set point of 1.5 nA and sample bias voltage of +2 V. The I-V characteristics have been recorded in the current imaging tunneling spectroscopy mode simultaneously with constant current image by the interrupted-feedback-loop technique. Each of the I/V characteristics has been recorded for both polarities in the ±2 V range for 40 discrete voltage steps at time interval of 0.02 s per step. The I/V characteristics have been stored in a computer and the first derivative dI/dV calculated. The dI/dV is a measure of local density of states (LDOS).

The surface has been scanned again after each of the experiments using constant current mode, sample bias of +0.2 V and current set point of 1.5 nA, searching for any damages of the surface caused by the spectroscopy measurements that may take place at higher voltages, which can appear during tunneling spectroscopy. In the case of visible damages, the spectroscopy data has been discarded.

The evolution of spectroscopic curve dI/dV recorded along CN is presented in Fig. 12. The spectra differ essentially from that recorded over the pure graphite region. The very low density of states in the Fig. 12a diagram indicates that the nanotube is semiconducting. The maxima of LDOS located at about 0.44 eV (V1), 1.23 eV (V2), 1.89 eV (V3) below and at 0.33 eV (C1), 1.00 eV (C2), 1.75 eV (C3) above the Fermi level are well resolved. We tentatively ascribe the peaks to the van Hove singularities of the LDOS.

![STM images of nanotubes adsorbed on the HOPG substrate: a) open end multi wall CN (75.4*75.4 nm²) and b) closed end single wall CN (56*83 nm²).](image1.png)

![Figure 12. Evolution of the band structure in CN observed by tunneling spectroscopy dI/dV measurements. The first plot is recorded far from the cap (a); second close to the cap (b) and the third at the cap. The CN appears to be a semiconducting one with the band gap equal to ΔE_{semi}=0.77eV. Valence and conduction singularities are denoted by V1, V2, V3 and C1, C2, C3 respectively.](image2.png)
Within a simple tight-binding model of the semiconducting tube the band gap is given by \( \Delta E_{\text{semi}} = 2 \gamma a / D \), where \( a \) is the nearest-neighbor carbon-carbon distance equal 1.42 Å, \( D \) is the tube diameter and \( \gamma \) denotes the \( \pi - \pi \) energy overlap between neighboring carbon atoms equal to 2.9 eV. With the tube diameter of 10.5 Å obtained from the STM profile, one gets \( \Delta E_{\text{semi}} \approx 0.78 \) eV very close to the width of the plateau 0.77 eV observed experimentally. The observed diameter of the tube may differ from the actual dimensions for the interaction with the substrate can influence the line profile, it may also lead to mechanical deformations of the tube.

Evolution of \( dI/dV(V) \) along the nanotube suggests change of conductivity from semiconducting to metallic at approaching the cap if the results were interpreted in terms of the band calculations. However, the molecular approach to the density of states singularities observed at the ends of any CN seems to be more appropriate. Thus, the peak observed at the tube’s cap denoted by RS in Fig. 12c indicates one of the occupied states shown in Fig. 9 and 10.

5. Concluding remarks

Fullerenes proved to be very interesting new form of pure molecular carbon. The efficient methods of fullerenes production made them easily accessible for many experiments. Properties of fullerenes may be modified by chemical methods because many reactions have been found to produce various fullerene based compounds. In chemistry, fullerenes play a role of functional groups carriers. They readily form adducts as well as charge transfer complexes. These processes allow modifying solids based on fullerenes.

Carbon nanotubes are natural one-dimensional wires and the strongest wear resistant fiber. The experiments show that existing theoretical models adequately describe properties of CN. Macroscopic amounts of CN are also easily available however, growth processes do not allow for control of the product properties. There also do not exist efficient methods of selection of samples exhibiting desired properties.

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